DYNAMIC MECHANICAL PROPERTIES OF EPOXY-POPLAR COMPOSITE MATERIALS

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ABSTRACT

The effects of impregnation on the dynamic mechanical properties of yellow-poplar (*Liriodendron tulipifera* L.) sapwood have been investigated for stoichiometric and nonstoichiometric mixtures of a diglycidyl ether of bisphenol-A based epoxy resin and meta-phenylenediamine. For the temperature range from 0 to 100 C, the measured values for the dynamic modulus of these wood-polymer composites exceeded the predicted values based upon the rule of mixtures. In contrast, the actual results for the internal friction values were significantly lower than those predicted by the rule of mixtures. Modification of this equation for strain energy sharing effects resulted in much improved estimates for the internal friction values, however.

Keywords: Dynamic mechanical properties, epoxy, impregnation, wood-polymer composites.

INTRODUCTION

There are three basic ways in which synthetic polymers can combine with wood to form a composite material. First, the polymer can be in a continuous film form, such as an adhesive for plywood or as a coating protecting a wood substrate. Second, the polymer can act as a matrix for wood in a comminuted form such as in particleboard or wood flour-filled phenolics. And third, the void spaces of whole wood or a reconstituted wood product can be partially or completely filled with polymer. This third type of composite is called polymer-impregnated wood, and it is the topic of the present study.

A number of articles have been published in past years dealing with polymer-impregnated wood and wood products. Many monomers and polymers have been studied as impregnants—including methyl methacrylate, styrene, styrene plus acrylonitrile, polyester plus styrene, urethane, epoxy, vinyl chloride, ethyl acetate, vinyl acetate, polyethylene glycol, and phenol formaldehyde. Of these, methyl methacrylate has received the most detailed attention. Many species of wood have been impregnated, along with reconstituted products such as flakeboard,

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particleboard, hardboard, and barkboard. Review articles emphasizing the industrial applications of these products are available (Meyer 1977; Meyer 1982).

In multiphase systems such as polymer-impregnated wood, one is frequently concerned with the relationship between the properties of the composite and the properties of the individual components. It has been reported (Siau et al. 1968) that many properties of polymer-impregnated wood follow the rule of mixtures:

$$P_c = P_m V_m + P_w \quad (1)$$

where P is the property of interest, V is the volume fraction, and the subscripts c, m, and w refer to the composite, the impregnant, and the gross wood, respectively. In work involving methyl methacrylate- and styrene-impregnated basswood (*Tilia sp.* L.), Siau et al. (1968) reported that most static properties in bending and compression apparently followed the above relationship, but the room temperature dynamic mechanical properties (DMP) in bending did not. Specifically, the rule of mixtures resulted in conservative estimates of the dynamic modulus, accounting for only about two-thirds of the observed change due to impregnation. For the damping, on the other hand, the predicted values were much higher than the observed values. These effects are intriguing, since one might normally expect deviations from the static properties rather than the dynamic properties because of the much lower strain levels employed in the measurement of the latter.

It is apparent that the dynamic mechanical behavior of polymer-impregnated wood remains to be explained. An effective method of examining these systems is to measure their behavior as a function of temperature, and, in particular, over a range in which the properties of the wood substrate are not a strong function of the temperature but those of the impregnant are. In this way, one can better examine the influence that the impregnant has over the composite.

The dynamic mechanical response of unimpregnated wood is generally considered to be a strong function of both temperature and moisture content. However, it has been shown by several investigators (Blankenhorn 1972; Kline et al. 1972), that the internal friction and dynamic elastic modulus of various oven-dry species are relatively passive in the temperature range from 0 to 100 C. Thus, these represent convenient conditions for further study.

The selection of an impregnant that is active in this temperature range is a critical task, and one that could be formidable as well, since thousands of polymers have been patented in the U.S. alone. Ideally, the choice of an impregnant should be based solely upon the relative ease with which its properties can be tailored in the 0 to 100 C range; but there are other practical considerations. These include an ability to penetrate the wood, a nonswelling nature, an ability to bond to the cell wall, and low shrinkage during polymerization. Epoxies would seem to be ideal impregnants on the basis of most of these criteria, especially since their properties are strong functions of stoichiometry and can be readily manipulated in the laboratory. Stoichiometric and nonstoichiometric mixtures of diglycidyl ether of bisphenol-A and meta-phenylenediamine, for example, have been shown by Kreahling and Kline (1969) to be strong functions of temperature in the 0 to 100 C range. Their drawback is that the predominant diglycidyl ethers of bisphenol A varieties are extremely viscous, and would require diluents in order for use in wood. Since the effects of diluents on the dynamic mechanical

properties of wood are largely unknown (Blankenhorn 1972; Sadoh 1981), their presence would complicate the analysis. A recently developed technique (Moore et al. 1983), however, permits the use of high viscosity epoxies as impregnants without diluents in a variety of species including yellow-poplar, red maple, birch, and red oak.

For the present study, systems consisting of oven-dry yellow-poplar (*Liriodendron tulipifera* L.) impregnated with stoichiometric and nonstoichiometric mixtures of Epon 828* and meta-phenylenediamine curing agent were selected. The DMP in bending of these systems from 0 to 100 C is described in detail. The applicability of the rule of mixtures to the dynamic elastic modulus and to the internal friction is also examined, and reasons for deviation from this predicted behavior are discussed.

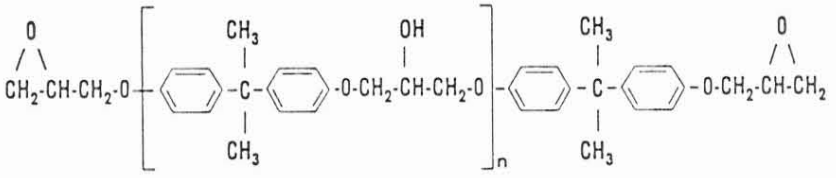
EXPERIMENTAL

Wood specimens

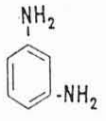
All samples were cut from a yellow-poplar (*Liriodendron tulipifera* L.) log approximately 69 cm in diameter, which was purchased from a local supplier in central Pennsylvania during the winter of 1979. This log was livesawn into $^5/_4$-in. × 6-in. × 8-ft boards, which were then kiln-dried in a mixed load using standard kiln-drying procedures. One clear board containing a large proportion of sapwood was chosen, and jointed, planed, and ripped into 0.95- × 0.95-cm strips. Straight grain portions of the sapwood strips were then turned and faced on a lathe to produce dowels having a diameter of 0.64 cm and a length of approximately 10.8 cm. These specimens were then machined slightly flat on the radial faces in order to prevent interference from side resonances during the DMP measurements (Moore 1981). A total of nine samples were machined, tested, impregnated, and retested as outlined in Fig. 1.

Impregnants

The epoxy resin used in the present study is Epon 828, whose structure is the following ($n < 1$):



This resin is mixed and reacted with varying amounts of meta-phenylenediamine (mPDA) curing agent:



* Epon 828 is a Shell Chemical Co. product.

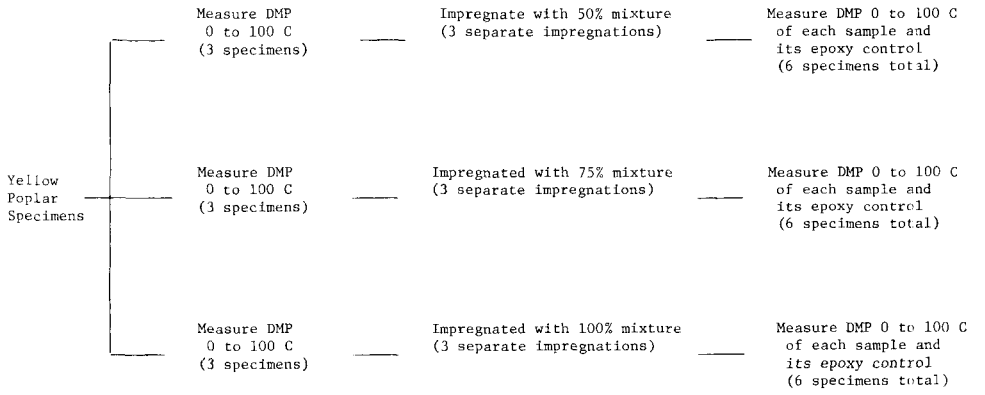


FIG. 1. Experimental design.

The amount of meta-phenylenediamine added to the epoxy resin is typically expressed as a percentage of the stoichiometric requirement. Since the functionalities of the resin and the curing agent are 2 and 4, respectively, in the polymerization process, the stoichiometric requirement is 14.1 parts by weight of meta-phenylenediamine per 100 parts by weight of resin (phr). In this study 50%, 75%, and 100% of the stoichiometric amounts were used, which correspond to 7.0, 10.6, and 14.1 phr, respectively.

Impregnant control specimens

All epoxy samples utilized in this study were cast as bars (0.635 cm wide, 0.635 cm thick, and 12.7 cm long) in silicone rubber molds. Since the resin and curing agent mixtures were cast at approximately 80 C, visible bubble or void problems were absent. Once cast, the samples were allowed to cure for 24 hours at 23 C, followed by 24 hours at 52 C and then 24 hours at 105 C. The intermediate (52 C) step was necessary to prevent surface defects.

The samples produced by this casting procedure had concave top surfaces associated with surface tension. This surface was ground parallel to the opposite side prior to use, and a sufficient amount of material was removed to ensure that the cross section was rectangular rather than square. As in the case of the wood specimens, this was necessary to avoid interference from side resonances in the dynamic mechanical property measurements.

Impregnation procedure

A vacuum-pressure-soak method was used to impregnate the wood samples with the above-described system. The wood specimens were oven-dried to constant weight at 105 C prior to being placed in the vacuum-pressure chamber. A vacuum of approximately 200 microns (2.7×10^{-3} kPa) was developed over the specimens, after which the resin and curing agent mixture (at approximately 80 C) was introduced into the chamber. Air was then bled into the chamber to return it to atmospheric pressure, and an overpressure of 200 psig (1,379 kPa) was then applied using nitrogen gas. This pressure was held for 2 hours, and then released over a period of about 20 minutes. The samples were removed from the chamber

and wiped free of excess resin. They were then heat-treated using the cycle detailed previously for the cast epoxy control samples. The details of this impregnation procedure and its effectiveness in impregnating yellow-poplar sapwood and a variety of other species have been summarized elsewhere (Moore 1981; Moore et al. 1983).

Dynamic mechanical property measurement

Measurements of the dynamic modulus (E′) and the internal friction (Q^{-1}) were made as a function of temperature on the apparatus desribed by Kline (1956) and later used by Bernier and Kline (1968) and Blankenhorn (1972). This is a nondestructive test that enables an experimenter to accumulate a large amount of data on a given specimen, both before and after treatment, without destroying the sample.

In this apparatus, the specimen is suspended by two cotton strings located outside of the nodes of the fundamental mode of vibration. One of the strings is attached to a biased magnetostrictive transducer that vibrates the sample as a beam at audio frequencies. The other string is connected to a piezoelectric crystal pickup device that converts the specimens vibrational response into an electrical signal.

The dynamic modulus (E′) is a function of the basic geometry of the sample, its mass, and its resonant frequency. The precision of the calculated values for E′ is ±0.3% at room temperature. Calculated values for E′ at higher and lower temperatures are obtained using room temperature dimensions, so their values are nominal. Within the range examined, however, the error introduced by this approximation is small compared to the observed temperature effects.

The internal friction is determined from the width of the resonance curve at the half power (3 db) level, and is expressed as:

$$Q^{-1} = \frac{\Delta f}{fo} \tag{2}$$

where Δf is the half power width and fo is the resonant frequency of the sample. For values of the magnitude of those observed in the present study, the above relationship is approximately equivalent to the product of π^{-1} and the logarithmic decrement. The precision of the internal friction measurements is only ±3%, largely because of the loss of significant figures that occurs in the Δf term. Further details concerning the apparatus and its construction are given by Kline (1956).

RESULTS AND DISCUSSION

Unimpregnated yellow-poplar

Figure 2 is typical of the results obtained for the dynamic modulus and the internal friction of oven-dry yellow-poplar sapwood from 0 to 100 C. These results are generally consistent with those reported by Blankenhorn (1972) for black cherry (*Prunus serotina* Ehrh.) and Kline et al. (1972) for white ash (*Fraxinus americana* L.). In general, the region from 0 to 100 C is a relatively uneventful one for oven-dry wood. The gradual decline in the internal friction is probably the tale of an extremely low and broad peak centered about −53 C, which has

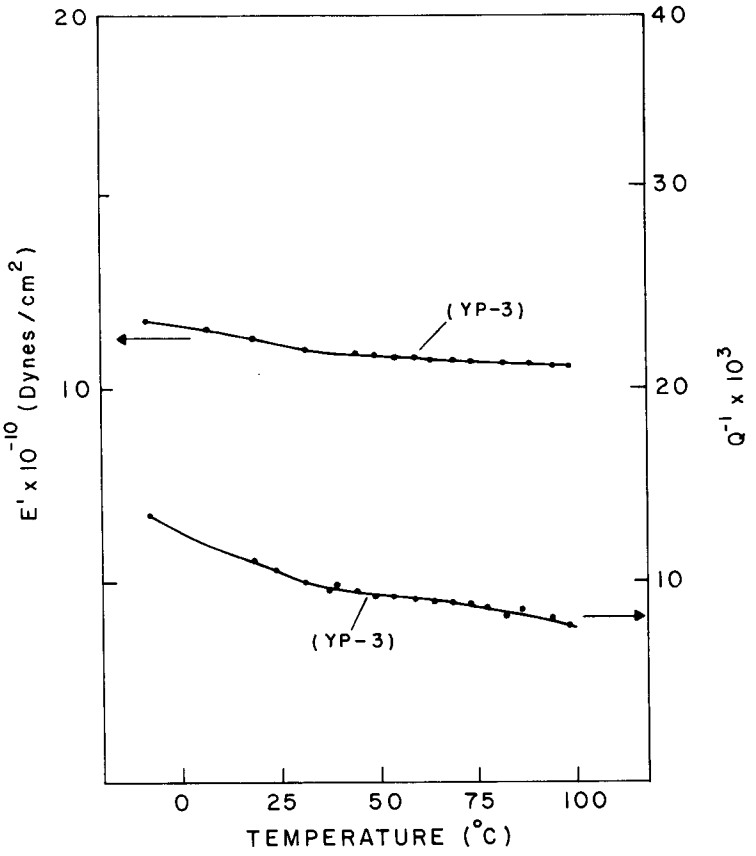


FIG. 2. Dynamic mechanical properties of oven-dry yellow-poplar sapwood.

been observed in several other species. The moisture sensitive nature of this peak has been investigated by Blankenhorn (1972) and Sellevold et al. (1975).

While the results varied somewhat among the nine specimens of yellow-poplar sapwood utilized (Table 1), the general trend illustrated in Fig. 2 is approximately the same for each specimen. Much of the observed variability in the dynamic modulus is related to the variation in gross oven-dry density (0.40 to 0.44 grams/cm^3). This relationship is well known (Kollmann and Côté 1968). In general, the internal friction data exhibit more variation than the dynamic modulus data as a function of temperature for a given sample. This is typical for the apparatus, because of the different natures of the two properties. Duplicate scans on specimen YP-3 illustrate the relative reproducibilities of the measurements.

Cured epoxy resins

Figure 3 illustrates typical results obtained for the dynamic modulus and internal friction as a function of temperature for Epon 828 cured with 50, 75, and 100% of the stoichiometric amount of meta-phenylenediamine. These results are

TABLE 1. *A summary of the dynamic mechanical properties of oven-dry yellow-poplar sapwood.*

Specimen	Density (grams/cm³)	$E' \times 10^{-10}$ (dynes/cm²)					$Q^{-1} \times 10^{3}$				
		0 C	20 C	50 C	80 C	100 C	0 C	20 C	50 C	80 C	100 C
YP-1	0.43	11.5	11.3	10.9	10.7	10.6	13.6	12.1	10.4	9.6	9.0
YP-2	0.41	11.0	10.7	10.4	10.3	10.1	12.7	11.7	9.1	8.7	9.4
YP-3	0.43	11.6	11.3	11.0	10.8	10.6	12.6	11.3	9.6	8.7	8.0
YP-3	(rerun)	11.6	11.3	10.9	10.8	10.6	11.5	10.8	9.5	9.5	9.2
YP-4	0.42	12.7	12.3	11.9	11.7	11.6	12.0	10.7	9.7	10.3	12.7
YP-5	0.43	12.2	11.8	11.4	11.2	11.2	11.9	10.8	9.3	8.5	8.0
YP-6	0.42	11.1	10.8	10.3	10.2	10.0	12.8	10.8	10.0	10.5	11.4
YP-7	0.43	11.3	11.0	10.6	10.4	10.3	12.9	11.4	9.6	8.6	7.7
YP-8	0.40	10.8	10.6	10.3	10.1	10.0	14.4	13.2	12.0	11.7	11.0
YP-9	0.44	12.3	11.9	11.6	11.3	11.2	13.3	12.1	9.8	8.4	8.4

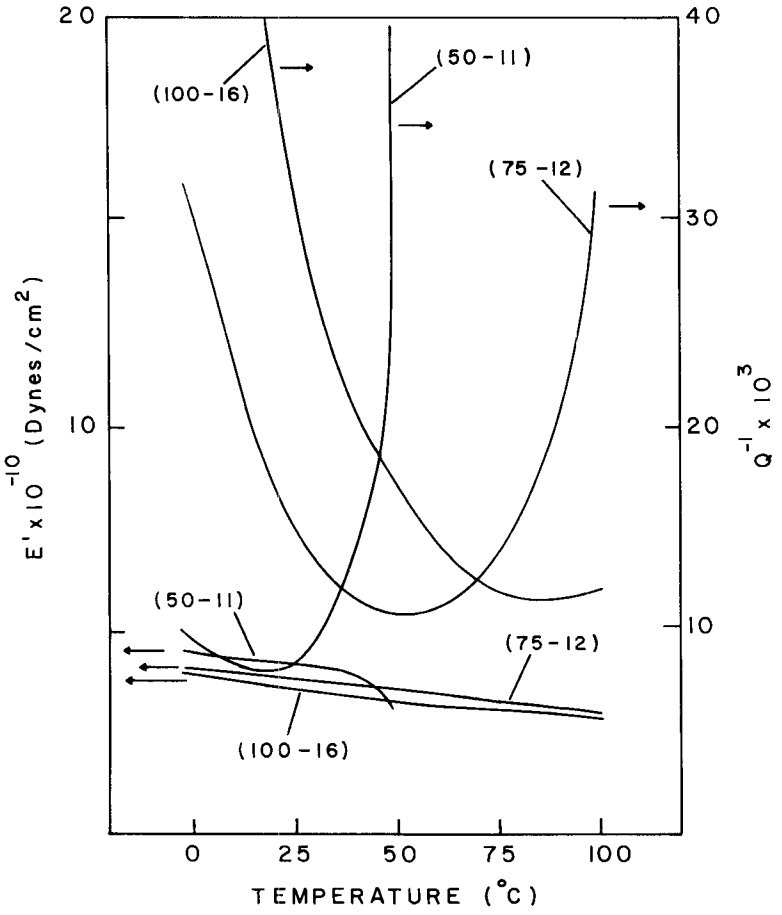


FIG. 3. Dynamic modulus and internal friction of epoxy resin mixed with 50, 75, and 100% of the stoichiometric amount of curing agent.

TABLE 2. *A summary of the dynamic mechanical properties of epoxy resin cured with 50, 75, and 100% of the stoichiometric amount of curing agent.*

Specimen	Stoichiometry (%)	Oven-dry density	$E' \times 10^{-10}$ (dynes/cm^2)					$Q^{-1} \times 10^3$				
			0 C	20 C	50 C	80 C	100 C	0 C	20 C	50 C	80 C	100 C
50-5	50.0	1.18	4.2	4.0	3.0	N.D.	N.D.	8.4	6.9	56.6	N.D.	N.D.
50-11	50.4	1.17	4.4	4.2	3.2	N.D.	N.D.	9.7	7.8	52.8	N.D.	N.D.
50-17	50.0	1.18	4.7	4.4	3.5	N.D.	N.D.	11.9	11.0	46.7	N.D.	N.D.
75-7	74.8	1.19	4.2	3.9	3.6	3.3	2.9	30.2	21.1	12.4	15.1	32.6
75-7 (rerun)	74.8	1.19	4.2	4.0	3.6	3.2	2.9	29.2	17.6	10.3	14.5	28.8
75-13	75.0	1.18	4.1	3.8	3.5	3.2	2.8	31.1	18.1	11.1	15.3	30.8
75-17	75.0	1.18	4.1	3.8	3.5	3.2	2.9	33.1	21.5	13.6	16.4	31.9
100-13	99.5	1.19	4.0	3.6	3.2	3.0	2.8	52.1	35.9	16.6	11.8	11.8
100-16	100.0	1.18	4.0	3.6	3.2	3.0	2.8	53.2	38.1	18.8	11.4	11.7
100-16 (rerun)	100.0	1.18	3.9	3.6	3.2	3.0	2.8	50.2	36.9	17.1	11.7	11.9
100-22	99.3	1.18	3.9	3.5	3.2	2.9	2.8	51.4	35.6	18.8	12.4	11.7

consistent with more extensive work reported by Kreahling and Kline (1969) for similar systems. The rather pronounced relaxation processes beginning at about 25 C for the 50% of stoichiometric specimens, and at about 55 C for the 75% of stoichiometric specimens are associated with the onset of the glass transitions of these samples. The glass transition of the 100% of stoichiometric specimens is well above 100 C (Kreahling and Kline 1969). This change in glass transition temperature with percentage of stoichiometry is presumably due to the change in segment mobility that results from the greater concentration of tetrafunctional units at higher stoichiometries. The processes observed at temperatures below the onset of these glass transitions are presumably parts of large, low temperature internal friction peaks centered between 100 and 300 K. As noted by Kreahling and Kline (1969), these peaks are sensitive both to stoichiometry and to heat treatment. They are thought to be related to either a crankshaft motion of the following segment (May and Weir 1962):

$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH-O-$$

formed during the polymerization process, or to rotation of the bisphenol A segment about the ether linkages (Cuddihy and Moacanin 1970).

An interesting result of the variation in stoichiometries is the difference in moduli at a given temperature. One typically associates higher moduli with higher crosslink densities. In the present study, however, the lowest stoichiometry mixture (lowest crosslink density) possesses the highest modulus in the range from approximately 0 to 30 C. This result has also been noted by Kreahling and Kline (1969) for mixtures of diglycidyl ether of bisphenol A and meta-phenylenediamine, and by Hirai and Kline (1972) for mixtures of Epon 828 and diethylenetriamine. This effect is apparently limited to a relatively narrow temperature range, although Hirai and Kline (1972) found a correlation between the modulus and the density at 24 C. In contrast to the modulus trend, the strengths of these materials at room temperature are lowest for the stoichiometries that have the highest moduli. No explanation is currently available for these effects. Table 2

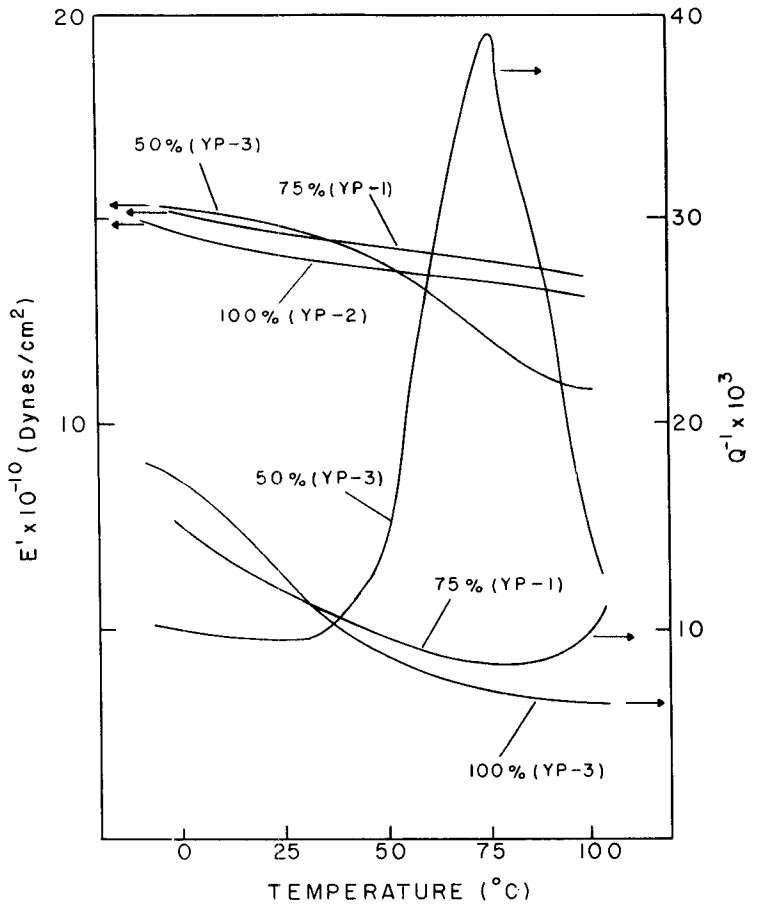


FIG. 4. Dynamic modulus and internal friction of yellow-poplar sapwood impregnated with mixtures of epoxy resin and 50, 75, and 100% of the stoichiometric amount of curing agent.

summarizes the dynamic mechanical properties of the specimens. Each was mixed and cast from a separate batch and is the control for a specific replication in the impregnation portion of this study.

Impregnated yellow-poplar

The impregnation procedure resulted in impregnant volume fractions of approximately 0.6 for each of the yellow-poplar samples in this study. Actual values ranged from 0.55 to 0.64, and this variation was related to the differences in oven-dry density of the substrates. All specimens were dissected and examined after testing, and the impregnant in each case appeared to be uniformly distributed throughout the lengths and cross sections.

Figure 4 shows typical results for the dynamic modulus and the internal friction from 0 to 100 C for several of these impregnated yellow-poplar samples. Three samples, each representative of a different stoichiometry are illustrated. Results

TABLE 3. *A summary of the dynamic mechanical properties of impregnated yellow-poplar sapwood.*

Specimen	Impregn. stoich.	m	Impregn. control	Oven-dry density (g/cm³)	E′ × 10^{-10} (dynes/cm²)					Q^{-1} × 10^3				
					0 C	20 C	50 C	80 C	100 C	0 C	20 C	50 C	80 C	100 C
YP-1	74.8	0.62	75-7	1.16	15.2	14.8	14.4	14.0	13.6	15.5	13.8	9.9	8.5	9.0
YP-1 (rerun)	74.8	0.62	75-7	1.16	15.3	14.9	14.4	14.0	N.D.	14.7	11.9	8.6	7.1	7.3
YP-2	99.5	0.55	100-13	1.07	14.8	14.3	13.8	13.5	13.2	17.6	13.9	8.8	6.6	6.4
YP-3	50.0	0.61	50-5	1.15	15.4	15.0	14.1	11.8	11.0	10.0	9.2	14.3	38.2	14.0
YP-4	50.4	0.59	50-11	1.12	16.2	15.9	14.9	13.2	12.0	N.D.	N.D.	N.D.	N.D.	13.3
YP-5	100.0	0.64	100-16	1.18	15.7	15.1	14.6	14.2	14.0	17.4	14.0	8.9	6.8	6.4
YP-6	75.0	0.60	75-10	1.13	14.2	13.8	13.3	12.8	12.4	14.0	11.2	8.5	8.9	10.8
YP-7	99.3	0.57	100-22	1.09	14.3	13.8	13.3	12.9	12.7	18.4	15.4	10.4	8.7	8.2
YP-8	50.0	0.59	50-17	1.10	14.3	14.1	13.2	N.D.	10.3	N.D.	N.D.	N.D.	N.D.	10.1
YP-9	75.0	0.55	75-17	1.09	15.4	15.0	14.5	14.1	13.8	16.1	15.0	13.2	10.4	10.0

are similar for the remaining samples, and Table 3 summarizes the data for all nine impregnated samples.

A close examination of Fig. 4 and Table 3 indicates that both the dynamic modulus and the internal friction are strongly influenced by the stoichiometry of the impregnant. In particular, the properties of the specimens impregnated with the mixture containing 50% of the stoichiometric amount of curing agent (YP-3, YP-4, YP-8) are drastically different from those with higher stoichiometries. This is not surprising in view of the significant changes in dynamic mechanical properties that can occur in the glass transitions of amorphous polymers such as epoxies.

While the dynamic mechanical properties of the impregnated specimens show characteristics of both the yellow-poplar substrate and the impregnant, they do not behave according to the rule of mixtures. For each specimen in this study, the rule of mixtures explains only about two-thirds of the observed increase in dynamic modulus in the temperature range examined. On the other hand, the predicted values for the internal friction are much higher than the actual values. These effects are illustrated in Fig. 5 (dynamic modulus) and Fig. 6 (internal friction) for a yellow-poplar specimen impregnated with a mixture of Epon 828 and 100% of the stoichiometric amount of meta-phenylenediamine. Data for the wood prior to impregnation and for the cast epoxy control sample are also included on these two figures for comparative purposes.

As noted in the introduction, there are few data available with which to compare these results. They do agree favorably with other findings (Siau et al. 1968) for impregnated basswood, although this is perhaps fortuitous considering the different natures of the impregnants. Siau et al. (1968) reported that the rule of mixtures accounted for only 53% of the observed increase in the room temperature modulus due to impregnation with methyl methacrylate and 73% with styrene. In the present case, the same relationship predicts about 64 to 71% of the observed increase, depending upon the stoichiometry. This confirms that these effects are also related to systems other than those which Siau et al. (1968) studied.

The internal friction results deviate even further from the rule of mixtures than

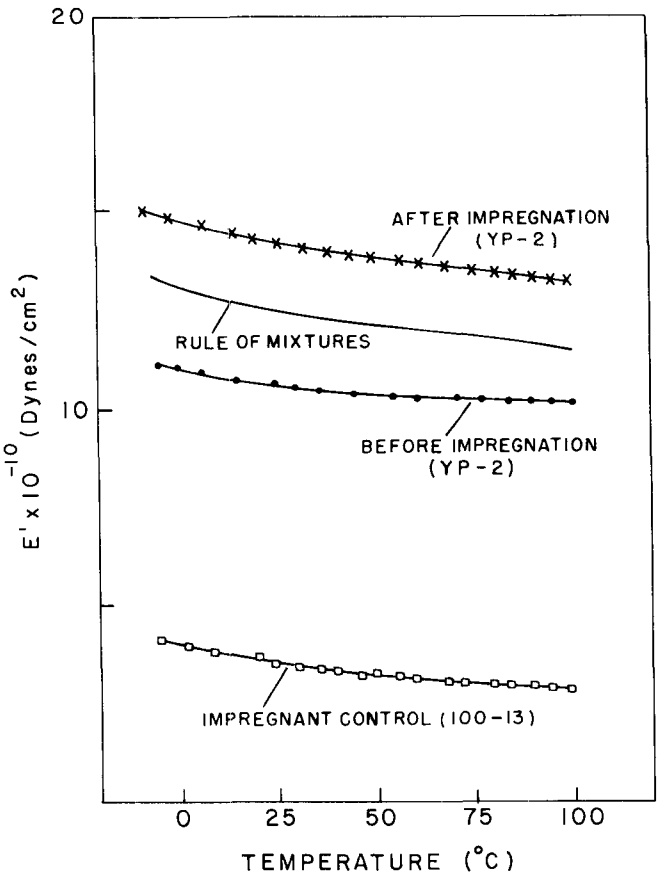


FIG. 5. Dynamic modulus of oven-dry yellow-poplar sapwood before and after impregnation with a mixture of epoxy resin and 100% of the stoichiometric amount of curing agent.

the dynamic modulus results. In all cases, the damping values of the composites are lower than the predicted values. Many contributing and competing factors not considered by the rule of mixtures could be involved. Nielsen (1974), for example, noted that in filled composites additional damping can occur because of slippage at the filler-matrix interface. It is unlikely that this type of effect occurs in epoxy-impregnated wood for several reasons. First, it is known that the wood substance has an affinity for both epoxies and amines (Rowell et al. 1976; Parham et al. 1972). Second, hydroxyl groups are known to accelerate the polymerization of epoxy resins (Bowen and Whiteside 1970). Because of these effects, it is likely that the impregnant is strongly bonded to the cell-wall surface. This would effectively eliminate or drastically reduce the equivalent of filler-matrix generated internal friction in epoxy-impregnated wood and could possibly have the opposite effect on internal friction by restricting certain molecular motions.

One could also speculate that one of the components of the mixture of epoxy resin and amine is preferentially absorbed in significant amounts by the wood substrate and removed from the polymerization reaction. This also is unlikely

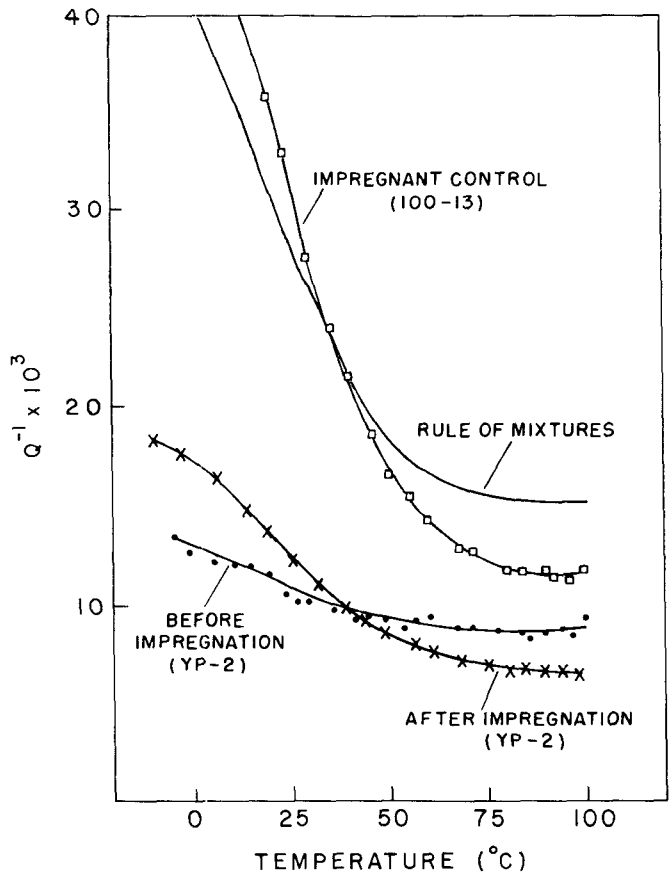


FIG. 6. Internal friction of oven-dry yellow-poplar sapwood before and after impregnation with a mixture of epoxy resin and 100% of the stoichiometric amount of curing agent.

because the internal friction curves for the composites show strong characteristics of the cast controls. Since the internal friction of the impregnant is a strong function of stoichiometry, it is unlikely that one of the components is preferentially excluded by the wood. The lack of any significant swelling is also consistent with these thoughts.

In addition to these effects, however, one could consider the possibility of strain energy sharing. If strong bonds do exist at the interface between the components, then the strain should be the same in both components when the composite is stressed. Since the moduli of the two components are different, the wood and the impregnant accept fractions of the total strain energy of the composite which are different from their volume fractions. Specifically, the material with the lower modulus accepts a proportion of the total strain energy which is lower than its volume fraction, while the material with the higher modulus accepts a portion which is greater than its volume fraction. In view of this, the internal friction of the composite can be better estimated by the following modified rule of mixtures (Moore 1981):

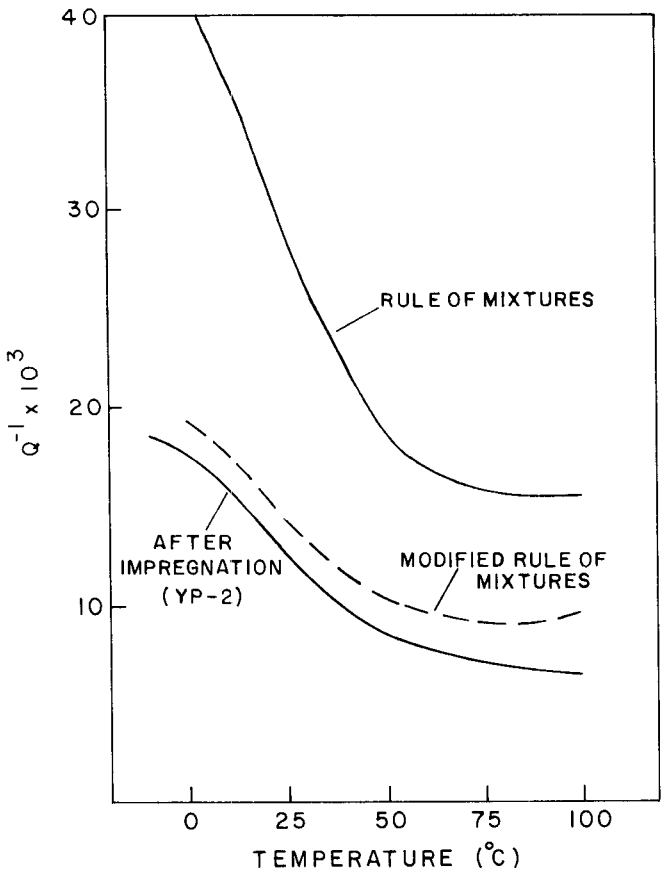


FIG. 7. Observed and predicted internal friction of yellow-poplar sapwood after impregnation with a mixture of epoxy resin and 100% of the stoichiometric amount of curing agent.

$$Q_c^{-1} = \frac{E_w}{E_c} Q_w^{-1} + \frac{E_m}{E_c} V_m Q_m^{-1} \quad (3)$$

where the symbols and subscripts are as defined previously. This is still an estimate, however, since strain energy sharing is a function of the actual moduli of the components of the composite. These values (as well as those for the internal friction) are not necessarily the same as those for the bulk materials. This is particularly true if the two components are strongly bonded to one another and certain molecular motions are hindered.

Figure 7 compares the observed internal friction values from 0 to 100 C for the impregnated yellow-poplar specimen (YP-2) illustrated previously in Figs. 5 and 6 with the predicted values using the rule of mixtures and the above modified form. Similar results are exhibited by the other specimens in this study. These show that the modified rule of mixtures provides much better estimates than the unmodified form. The estimates are still somewhat high, but this could be related either to the interfacial effects that were neglected in the derivation or to differences in the moduli of the components in the bulk and in the composite.

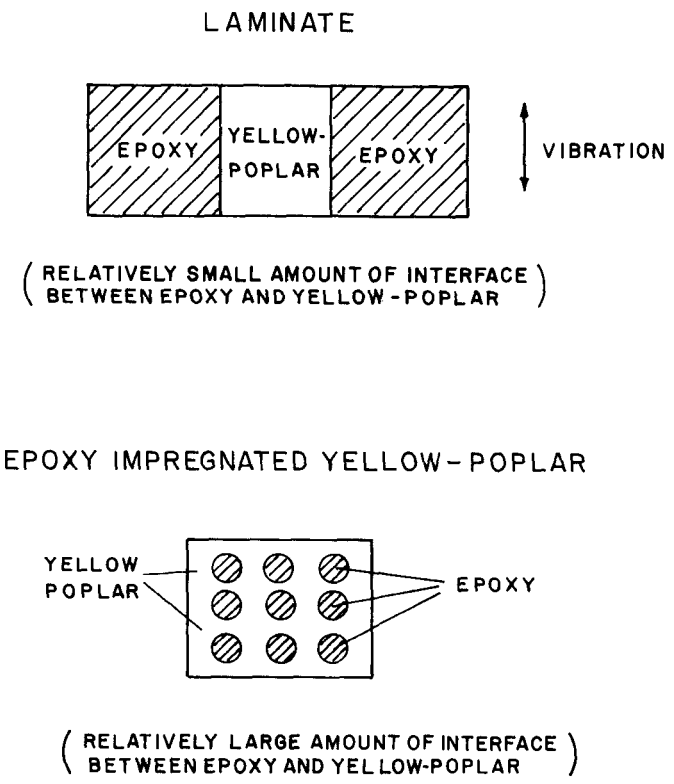


FIG. 8. Similar systems with different interfacial volume fractions.

While it is relatively easy to explain or justify differences between predicted and observed internal friction values for impregnated wood, the discrepancy between the observed and predicted moduli is more difficult. Siau et al. (1968) suggested that a significant degree of interaction occurs at the interface, which creates a stiffening effect (increased modulus) above the rule of mixtures prediction. A related explanation would seem to be that the interaction stabilizes a number of defect sites or weak points or slip planes in the structure which influence the modulus of the gross wood, thus yielding a higher effective modulus for this component.

In considering these thoughts, it is interesting to compare results for polymer-impregnated wood with those for a laminate of similar overall composition consisting of a small number of epoxy and yellow-poplar plies. These two systems are similar in many respects, but notably different in that the laminate contains a lower proportion (by volume) of interface between cell wall and epoxy (Fig. 8). Thus, the nature of the stabilization of the wood structure by the epoxy should be different in each case.

Two laminates were constructed during this study, each by gluing a piece of yellow-poplar sapwood (whose dynamic mechanical properties were also known) made from a mixture of Epon 828 and 75% of the stoichiometric amount of meta-

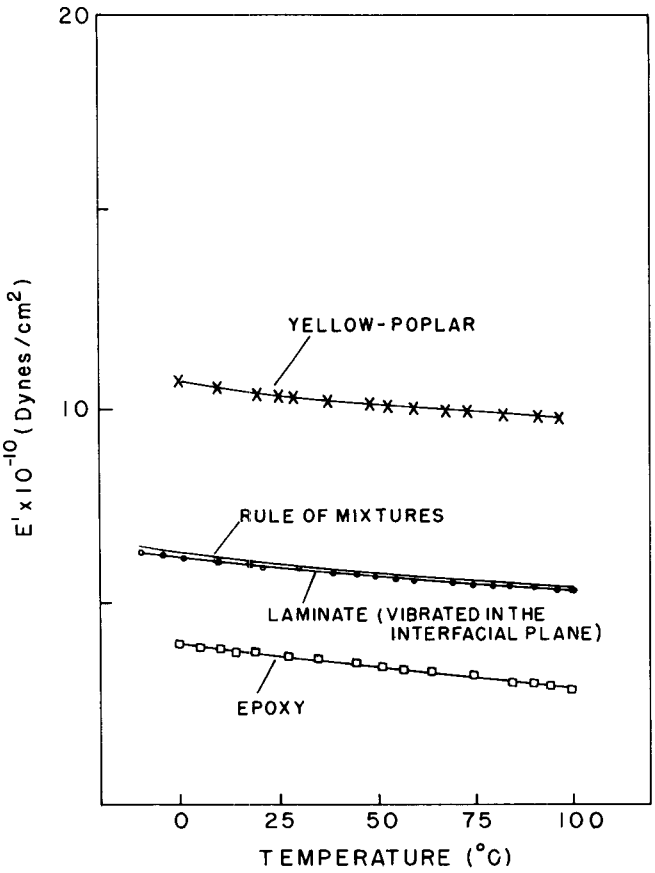


FIG. 9. Dynamic modulus of three-ply laminate containing yellow-poplar sapwood and epoxy (V_w = 0.35).

phenylenediamine. The adhesive's composition was the same as that of the cast epoxy specimens. The relative proportions of each component were chosen so that the volume fractions of epoxy were approximately 0.65 and 0.56 in the two samples.

Figure 9 illustrates the dynamic modulus from 0 to 100 C of one of these laminates. The dynamic moduli of the individual components are also included for comparative purposes, along with the rule of mixtures predictions. The agreement between the observed and predicted values is good, with the rule of mixtures accounting for about 98% of the observed changes in the moduli. Similar results were obtained for the other laminate. These data support the importance of the interface in determining the modulus of the composite.

An interesting contrast to the dynamic modulus is provided by the internal friction. Figure 10 shows the internal friction of the same laminate from 0 to 100 C, along with the values for the components and the predictions from the rule of mixtures and the modified rule of mixtures. The agreement for the modified form

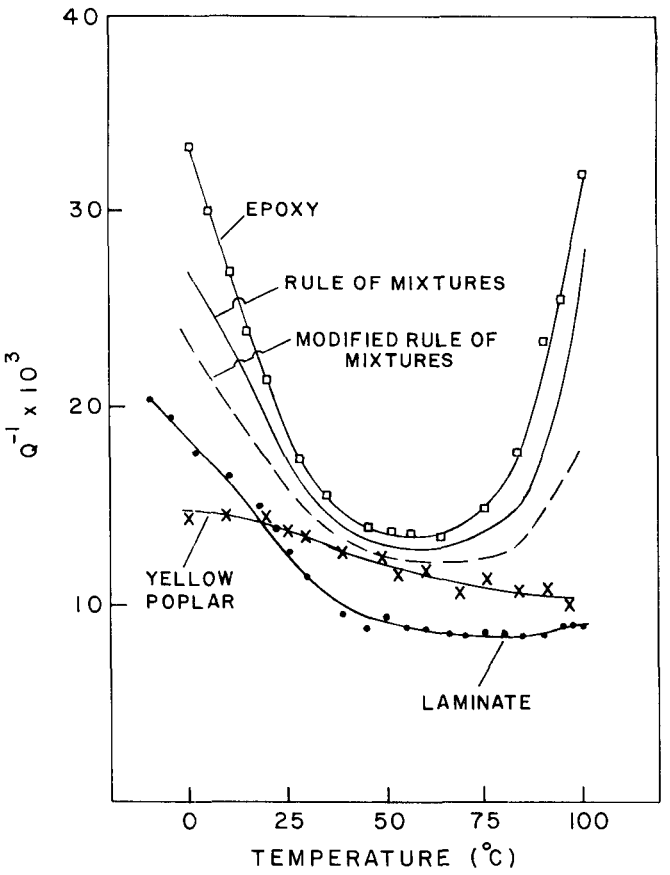


FIG. 10. Internal friction of a three-ply laminate containing yellow-poplar sapwood and epoxy ($V_w = 0.35$).

seems slightly better than that for the unmodified rule of mixtures, which suggests that strain energy sharing is important in systems with low proportions by volume of interface. In contrast to the results for the impregnated wood, however, it does not account for much of the observed change in internal friction. This further suggests that mechanisms other than those considered in the present study can be involved.

One possible explanation for this behavior leads to an interesting hypothesis. It is reasonable to assume that in the laminate (as opposed to in the impregnated wood) the epoxy can better stabilize the wood in a shear mode. This is because the polymer is continuous in the planes of shear strain in the laminate and discontinuous in the planes of shear strain in the impregnated wood (Moore 1981; Moore et al. 1983). As noted by Blankenhorn (1972), the contribution that shear makes to the internal friction in wood is not known. If this contribution is substantial, however, then the epoxy (because of its relatively high G) could reduce the contributions of various shear-related damping mechanisms in the

wood in the laminates. This would then explain the low observed values for the composite. This possibility will be considered in future work.

SUMMARY

Results have been presented to illustrate the influence of impregnation on the dynamic mechanical properties of yellow-poplar (*Liriodendron tulipifera* L.) sapwood. The properties of the impregnant were varied by adjusting the amount of meta-phenylenediamine during agent from 50 to 100% of the stoichiometric requirement. This permitted a thorough examination of the influence of the impregnant on the performance of the composites. It was found that the dynamic mechanical properties are sensitive to these changes in stoichiometry.

Under all conditions examined, the internal friction of the epoxy-impregnated poplar was significantly lower than the predictions of the rule of mixtures. After this equation was adjusted for estimated strain energy sharing effects, the predicted values for the impregnated wood were in much better agreement with the observed values. In contrast to the internal friction, the dynamic moduli of the impregnated composite materials exceeded the predictions of the rule of mixtures in all cases, and it was postulated that this could also be related to a high degree of interaction at the interface. Results for laminates having overall compositions similar to those of the impregnated yellow-poplar samples were presented that support his hypothesis.

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